

Chemical Modeling of Boron Adsorption by Humic Materials Using the Constant Capacitance Model

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Abstract: The constant capacitance surface complexation model was used to describe B adsorption behavior on reference Aldrich humic acid, humic acids from various soil environments, and dissolved organic matter extracted from sewage effluents. The reactive surface functional groups on the humic materials were assumed to be a carboxyl site, XOH, and a phenol site, YOH. Initially, total concentrations of the sites, XOH_T and YOH_T and the proton dissociation constants for the carboxyl site, LogK_{X-}, and the phenol site, LogK_{Y-}, were optimized by fitting the constant capacitance model to potentiometric titration data on reference Aldrich humic acid obtained from the literature. Subsequently, the model was fit to experimental B adsorption data obtained from the literature by optimizing two tetrahedral B surface complexation constants: LogK_{XB} for a carboxyl site and LogK_{YB} for a phenol site. The model was well able to describe the experimental B adsorption data both as a function of solution B concentration (isotherm data) and solution pH (envelope data) for all humic materials. The ability to represent changes in B adsorption as a function of solution pH is the main advantage of the constant capacitance model over adsorption isotherm equations. Results from the current study can be used to describe B adsorption behavior on diverse humic materials of interest in environmental and agricultural situations.

Key Words: Humic acid, B adsorption isotherm, B adsorption envelope (*Soil Sci* 2014;179: 561–567)

Boron is a micronutrient element required by plants in trace amounts that can become phytotoxic at elevated concentrations. The availability of B in soils is influenced by many soil factors, including organic matter content. In addition to the mineral constituents, oxides, clays, and carbonates, organic materials can act as sources and sinks for adsorbed B, as evidenced by highly significant correlations found between soil carbon content and B adsorption (Harada and Tamai, 1968; Elrashidi and O'Connor, 1982; Evans, 1987). Addition of external sources of organic matter increased B adsorption by soils for farmyard manure (Sharma et al., 2006) and composted organic matter (Yermiyahu et al., 1995).

Despite their small total content in most mineral soils, humic materials play an important role in B adsorption, retaining significant amounts of B (Parks and White, 1952). Bark compost exhibited a 10-fold greater B adsorption capacity than greenhouse soil (Van et al., 2005). Similarly, B adsorption by composted organic matter and humic acid on a weight basis was greater than B adsorption by clay minerals (Yermiyahu et al., 1988; Gu and Lowe, 1990; Lemarchand et al., 2005). The pH dependence of B adsorption on humic acids was similar to that exhibited on soil mineral

constituents. That is, B adsorption increased with increasing solution pH, exhibited an adsorption maximum near pH 9, and above pH 9 decreased with increasing solution pH (Gu and Lowe, 1990; Lemarchand et al., 2005). Parabolic pH dependence was also exhibited for B adsorption on plant cell wall materials, although the peak in adsorption was shifted to pH 10 (Goldberg and Grieve, 2003).

Historically, ion binding on humic substances has been described using models such as the Windemere Humic Aqueous Model (WHAM) (Tipping, 1994), the non-ideal competitive adsorption (NICA)–Donnan model (Kinniburgh et al., 1996), and the Stockholm Humic Model (SHM) (Gustafsson, 2001). The WHAM and SHM are discrete site models, whereas the NICA–Donnan is a continuous distribution model. In addition, all three models also consider ion association by electrostatic accumulation. So far, use of these models has been restricted to proton and metal adsorption. The number of adjustable parameters required to describe charging behavior of humic substances is six for the WHAM and SHM models and seven for the NICA–Donnan model.

Ligand exchange is a mechanism by which anions become adsorbed specifically in strong inner-sphere surface complexes containing no water between the adsorbing anion and the surface functional group. Yermiyahu et al. (1988) suggested ligand exchange with hydroxyl and carboxyl functional groups as the mechanism for B adsorption on organic matter. Using ¹¹B NMR, Lemarchand et al. (2005) observed chemical shifts corresponding to carboxylic and phenolic functional groups on humic acid. Using discrete site models containing either three sites (one carboxylic and two phenolic) or four sites (two carboxylic and two phenolic), these authors were able to describe B adsorption on humic acid as a function of solution pH and solution B concentration. The second carboxylic and phenolic sites were added to improve the quality of the model fit.

Boron adsorption on humic acid (Yermiyahu et al., 1988) and plant cell walls (Goldberg and Grieve, 2003) was found to increase with increasing solution ionic strength. Such behavior is caused by the greater activity of the background electrolyte ions in solution compensating for the surface charge generated by specific anion adsorption and is therefore indicative of inner-sphere surface complexation (McBride, 1997). The constant capacitance surface complexation model assumes specific inner-sphere surface complex formation via ligand exchange for anions. This model has been used successfully to describe B adsorption on plant cell wall materials as a function of solution pH assuming one phenolic site (Goldberg and Grieve, 2003). Boron adsorption on humic acid was represented as interactions with the phenol groups on catechol and described using the constant capacitance model as a function of equilibrium solution B concentration and solution pH (Meyer and Bloom, 1997).

An important advantage of the constant capacitance surface complexation model is consideration of the charge on both the adsorbing ion and the surface functional groups. The electrostatic potential term included in the model accounts for surface charge. The objectives of the present study were (1) to describe proton binding and obtain humic acid acidity constants using the constant

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Financial Disclosures/Conflicts of Interest: None reported.

Received August 21, 2014.

Accepted for publication December 29, 2014.

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ISSN: 0038-075X

DOI: 10.1097/SS.0000000000000098

capacitance model and (2) to test the ability of the constant capacitance model to describe B adsorption on a diverse set of humic acids and dissolved organic matter (DOM) as a function of solution B concentration and solution pH. This study will constitute the first test of the ability of a surface complexation model, the constant capacitance model, to describe B adsorption on a wide range of humic substances.

DATA AND METHODS

Model Formulation

The constant capacitance model (Stumm et al., 1980) is a chemical surface complexation model for proton binding and ion adsorption containing the following assumptions: (i) anion adsorption is based on a ligand exchange mechanism; (ii) all surface complexes are inner-sphere; (iii) surface complexes with the background electrolyte ions are not considered; (iv) a linear relationship exists between surface charge, σ ($\text{mol}_e \text{L}^{-1}$), and surface potential, ψ (V):

$$\sigma = \frac{CSC_p}{F} \psi \quad (1)$$

where C is the capacitance (F m^{-2}), S is the surface area ($\text{m}^2 \text{g}^{-1}$), C_p is the particle concentration (g L^{-1}), and F is the Faraday constant (C mol^{-1}).

The dissociation reaction for the surface carboxyl functional group, XOH, is:



and the dissociation reaction for the surface phenol functional group, YOH, is:

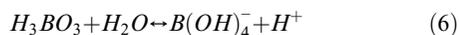


The surface complexation reactions for B adsorption are:



Consistent with the experimental B adsorption results of Lemarchand et al. (2005) on humic acid, only tetrahedral borate surface species are considered to form in the present study. This surface configuration is also in agreement with exclusively tetrahedral borate, and not trigonal boric acid, complexation to adjacent cis-diol hydroxyl groups observed on the sugar alcohol mannitol (Knoeck and Taylor, 1969). Consideration of monodentate B surface complexes is consistent with attenuated total reflectance–Fourier transform infrared spectroscopic results for B adsorption on amorphous Fe oxide (Peak et al., 2003). Bidentate B surface complexes have not yet been observed with spectroscopic experiments.

The constant capacitance model application contains the solution speciation reaction for boric acid, $\text{pK}_a = 9.24$:



The dissociation constants for the carboxylic and phenol functional groups are:

$$K_{X^-}(\text{int}) = \frac{[\text{XO}^-][\text{H}^+]}{[\text{XOH}]} \exp(-F\psi/RT) \quad (7)$$

$$K_{Y^-}(\text{int}) = \frac{[\text{YO}^-][\text{H}^+]}{[\text{YOH}]} \exp(-F\psi/RT) \quad (8)$$

where R is the molar gas constant ($\text{J mol}^{-1} \text{K}^{-1}$), T is the absolute temperature (K), and square brackets represent concentrations (mol L^{-1}). The electrostatic potential term can be considered as a surface activity coefficient correcting for surface charge produced by charged surface complexes. The equilibrium constants for B surface complexation are:

$$K_{X^-}(\text{int}) = \frac{[\text{XH}_3\text{BO}_4^-][\text{H}^+]}{[\text{XOH}][\text{H}_3\text{BO}_3]} \exp(-F\psi/RT) \quad (9)$$

$$K_{Y^-}(\text{int}) = \frac{[\text{YH}_3\text{BO}_4^-][\text{H}^+]}{[\text{YOH}][\text{H}_3\text{BO}_3]} \exp(-F\psi/RT) \quad (10)$$

The mass balance expressions for the carboxyl functional group and the phenol functional group are:

$$\text{XOH}_T = [\text{XOH}] + [\text{XO}^-] + [\text{XH}_3\text{BO}_4^-] \quad (11)$$

$$\text{YOH}_T = [\text{YOH}] + [\text{YO}^-] + [\text{YH}_3\text{BO}_4^-] \quad (12)$$

where XOH_T is the total number of carboxyl surface sites, and YOH_T is the total number of phenol surface sites. The charge balance equation is:

$$\sigma = -[\text{XO}^-] - [\text{YO}^-] - [\text{XH}_3\text{BO}_4^-] - [\text{YH}_3\text{BO}_4^-] \quad (13)$$

The computer program FITEQL 4.0 (Herbelin and Westall, 1999) was used to fit proton binding constants to the humic acid potentiometric titration data of Lemarchand et al. (2005). The FITEQL computer code uses a nonlinear least-squares optimization routine to fit equilibrium constants to experimental data and contains the constant capacitance model of adsorption. Goodness-of-fit of the constant capacitance model application was evaluated using the overall variance, V_f in the difference in the material balance, Y , such that:

$$V_f = \frac{\text{SOS}}{\text{DF}} \quad (14)$$

where SOS is the weighted sum of squares of the residuals and DF is degrees of freedom. Subsequently, B surface complexation constants were fit to adsorption data sets for various humic acids and for DOM. The investigation of Lemarchand et al. (2005) is the only published study that describes both proton charging and B adsorption on a humic material.

Experimental Data Sets

Experimental B adsorption data on humic acids and DOM were obtained from the literature. Gu and Lowe (1990) extracted humic acid fractions from three British Columbia soils from contrasting environments. HA-1 came from the B_{hf} horizon of a Duric Ferrohumic podzol. Such podzols have a B_{hf} horizon that is more than 10-cm thick and contains more than 5% organic carbon and more than 0.6% pyrophosphate-extractable Fe + Al. HA-2 was obtained from the A_p horizon of a Humic Luvic Gleysol. These organic surface horizons are 15 cm thick or more with organic carbon content of 2% or more. The source of HA-3 was the A_h horizon of a Black Orthic Chernozem. The A horizon of these soils is darkened by organic matter and associated with subhumid

climates and grassland native vegetation (Soil Classification Working Group, 1998). Meyer and Bloom (1997) extracted humic acid from a Terric Borohemist. By definition, histosols contain more than 50% organic material in the upper 80 cm. Borohemists have a frigid temperature regime and moderately decomposed organic material. Terric Borohemists also have a mineral layer of 30 cm thick or more with an upper boundary in the control section (Soil Survey Staff, 1999). A reference humic acid from Aldrich was used by Lemarchand et al. (2005). Both potentiometric titration and B adsorption data are available for this material. Communar and Keren (2008, 2009) studied the B adsorption behavior of two DOM fractions isolated from treated sewage effluents. DOM-1 was obtained from a municipal wastewater treatment plant using activated sludge technology, whereas DOM-2 resulted from a plant using aeration technology.

RESULTS AND DISCUSSION

The first step in the modeling procedure was to describe proton binding by humic acid. This was accomplished using the acid-base titration data obtained by Lemarchand et al. (2005) for Aldrich humic acid. These authors had applied a discrete site model without explicit representation of electrostatic energy and considered the humic acid as an assemblage of either two sites (one carboxylic and one phenolic) or three sites (two carboxylic and one phenolic). They optimized the proton binding constants and the total concentration of protonable sites simultaneously and considered the fit “quite satisfactory” for the two-site model and “perfect” for the three-site model.

Reanalysis of the acid-base titration data with the constant capacitance model using the proton binding reactions defined by Eq.(2) for a carboxyl group and Eq.(3) for a phenol group and considering surface charging by inclusion of the electrostatic potential terms, $\exp(-F\psi/RT)$, produced a fit to the experimental data that was equally as “perfect” as the three-site fit of Lemarchand et al. (2005). A more quantitative description of fit quality is provided by the goodness-of-fit criterion, V_Y , as

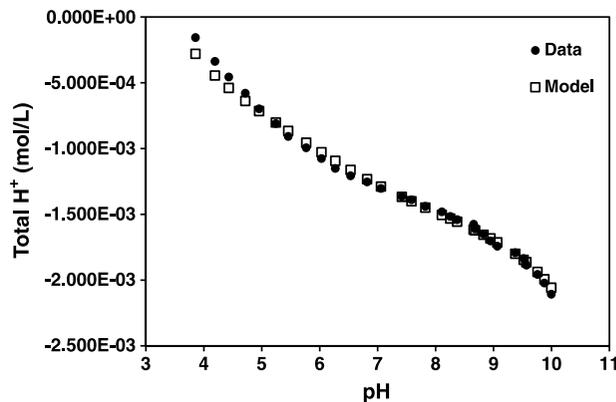


FIG. 1. Potentiometric titration of Aldrich humic acid. Experimental data from Figure 1 of Lemarchand et al. (2005) without CaCl_2 are represented by solid circles. Constant capacitance model results are represented by open squares.

indicated in Table 1. The constant capacitance model fit to the acid-base titration data is presented in Fig. 1. As had been done by Lemarchand et al. (2005), the total concentrations of surface sites were optimized simultaneously with the proton binding constants defined by Eq.(7) for the carboxyl group and by Eq.(8) for the phenol group. The constant capacitance model application was able to provide a fit of comparable quality to the nonelectrostatic discrete site model (Lemarchand et al., 2005) using one less adjustable acid dissociation parameter and including the chemically essential surface charging process. The total of four adjustable parameters needed in the constant capacitance model to describe charging of the humic acid also compares very favorably with the six adjustable parameters used by the WHAM and SHM models and the seven adjustable parameters used by the NICA-Donnan model.

Electrostatic effects have been included in previous descriptions of titration data for humic substances isolated from a lake

TABLE 1. Constant Capacitance Model Surface Complexation Parameters

	XOH_T , $\text{mmol}_c \text{ kg}^{-1}$	YOH_T , $\text{mmol}_c \text{ kg}^{-1}$	LogK_{X-}	LogK_{YX-}	LogK_{XB-}	LogK_{YB-}	V_Y
Lemarchand et al. (2005)							
HA titration	2,350	1,210	-3.28	-5.43			9.1
B adsorption f(pH)	235	121	-4.76	-10.68	-1.78	-5.04	362
B adsorption f(B_{eq})	235	121	-4.76	-10.68	-3.58	-5.98	27.8
Gu and Lowe (1990)							
B adsorption HA-1 f(pH, B_{eq})	138	69	-4.76	-10.68	-2.80	-5.25	197
B adsorption HA-2 f(B_{eq})	89.3	44.7	-4.76	-10.68	-2.77	-5.29	78.8
B adsorption HA-3 f(B_{eq})	48.7	24.3	-4.76	-10.68	-2.79	-4.90	186
Meyer and Bloom (1997)							
B adsorption f(pH, B_{eq})	100	50	-4.76	-10.68	-2.58	-4.35	131
B adsorption pH 8.7, 8.15, 6.73	100	50	-4.76	-10.68	-2.29	-4.55	75.8
Communar and Keren (2008)							
B adsorption DOM-1 f(B_{eq})	20.5	10.3	-4.76	-10.68	-2.92	-5.25	1.1
B adsorption DOM-2 f(B_{eq})	18.1	9.07	-4.76	-10.68	-2.59		3.4
Communar and Keren (2009)							
B adsorption DOM-2 f(pH, B_{eq})	1.55	15.2	-4.76	-10.68	-1.75	-5.34	43.7
Average					-2.58 ± 0.54	-5.11 ± 0.48	

Italicized values of reactive surface sites XOH_T and YOH_T were calculated as one tenth of the total number of reactive surface sites. Italicized values of LogK_{X-} and LogK_{YX-} were held constant during the optimization.

(Wilson and Kinney, 1977) and for Aldrich humic acid (Masini et al., 1998). The ion binding models WHAM (Tipping, 1994), SHM (Gustafsson, 2001), and NICA-Donnan (Kinniburgh et al., 1996) also include electrostatics. Masini et al. (1998) described their titration data by continuing to add carboxylic sites and phenolic sites to their model until no statistically significant improvement in fit was found. This produced three carboxylic sites ranging in pK_a value from 2.8 to 6.1 and three phenolic sites ranging in pK_a value from 7.4 to 9.9, a very large number of adjustable parameters. The dissociation constant values obtained by Wilson and Kinney (1977) for lake humic acids were $pK_a = 4.2$ for carboxyl and $pK_a = 8.1$ for phenol. The value of the dissociation constant for the carboxylic site obtained with the constant capacitance model, $pK_a = 3.28$, is consistent with the above literature values, falling within the range of Masini et al. (1998). The constant capacitance model value of the dissociation constant for the second site, $pK_a = 5.43$, falls below prior literature values for phenol sites. Thus, it is possible that the second dissociation constant obtained by the constant capacitance model may more correctly represent a second set of carboxyl sites. As had been indicated by Lemarchand et al. (2005), optimization of dissociation constants for phenolic sites is difficult because the highest titration data point in their data set is at pH 9.5.

Lemarchand et al. (2005) observed that the B adsorption capacity of their Aldrich humic acid was approximately one order of magnitude lower than the total concentration of protonable surface groups. Therefore, in describing their B adsorption data, Lemarchand et al. (2005) set the concentrations of carboxylic and phenolic groups at one-tenth the values optimized in describing their titration data. The pH-dependent B adsorption data set of Lemarchand et al. (2005) provided by far the most extensive coverage of data points over the pH range and was therefore used to reoptimize the carboxylic and phenolic acid dissociation constants. Lemarchand et al. (2005) had found it necessary to optimize an additional phenolic site to describe B adsorption, exhibiting an adsorption maximum around pH 10 because their potentiometric titration data were limited to pH values of 10 or less. For the same reason, the constant capacitance model was used to fit dissociation constants and B surface complexation constants for one carboxylic XOH site and one phenolic YOH site simultaneously. For all subsequent constant capacitance model applications to B adsorption, the dissociation constants were held fixed at these values: $\text{Log}K_{X^-} =$

-4.76 and $\text{Log}K_{Y^-} = -10.68$. These optimized values are very consistent with pK_a values of carboxyl and phenol groups, respectively. Figure 2 depicts the ability of the constant capacitance model to describe B adsorption as a function of solution pH (Fig. 2A) and as a function of equilibrium B concentration (Fig. 2B). The model was able to describe the experimental data of Lemarchand et al. (2005) both at low and high pH, as well as to match the pH of the B adsorption maximum (Fig. 2A) and to provide an excellent fit to the B adsorption isotherm data (Fig. 2B).

Gu and Lowe (1990) evaluated B adsorption behavior on three soil humic acids and described it using the Langmuir adsorption isotherm equation. Although they suggested that the constant capacitance model would be applicable to describe such B adsorption because phenol and hydroxyl groups of soil organic matter undergo ligand exchange and dissociation reactions, these authors chose not to fit the model to their data because of their limited number of data points. However, application of the constant capacitance model to these adsorption data was successful in the current study for all three humic acids. Both B adsorption isotherm (adsorption as a function of solution ion concentration) and B adsorption envelope (adsorption as a function of solution pH) data had been determined for HA-1 and were optimized simultaneously. Not only was the constant capacitance model fit to the B adsorption isotherm data at pH 6.7 and 8.8 comparable in quality to that previously obtained with the empirical Langmuir adsorption isotherm equation (Fig. 3A), but B adsorption as a function of solution pH was also described using the same two model B surface complexation constants (Fig. 3B). In this constant capacitance model application, two adjustable parameters were optimized: the tetrahedral B surface complexation constants, $\text{Log}K_{XB^-}$ and $\text{Log}K_{YB^-}$. Thus, using the same number of adjustable parameters, the constant capacitance model can provide chemical information that is lacking in the adsorption isotherm equation approach, such as consideration of the pH effect.

Meyer and Bloom (1997) applied the constant capacitance model to describe B adsorption by a humic acid extracted from a peat soil. They considered either the stability constant for B-catechol complexation to represent phenol sites or the stability constant for B-salicylate complexation to represent carboxyl sites. Using catechol sites, these authors were well able to describe B adsorption as a function of equilibrium B concentration at pH 8.7; underprediction was observed at pH 8.15 and pH 6.73. Although

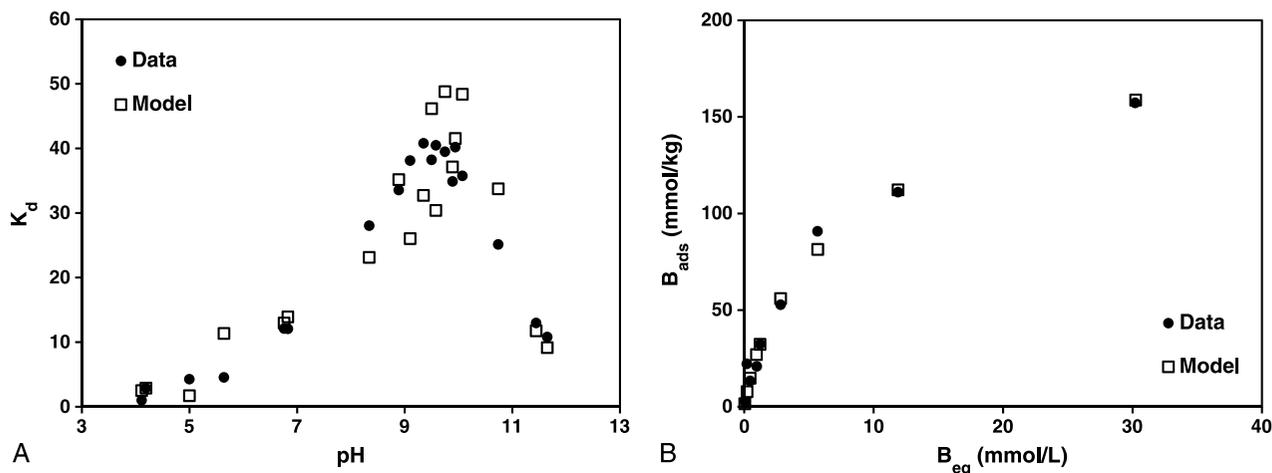


FIG. 2. Boron adsorption on Aldrich humic acid as a function of (A) solution pH and (B) equilibrium solution B concentration. Experimental data from Figures 2 and 3 of Lemarchand et al. (2005) are represented by solid circles. The B partition coefficient $K_d = (m_{B_{ads}}/m_{HA}) / (m_{B_{sol}}/m_{sol})$. Constant capacitance model results are represented by open squares.

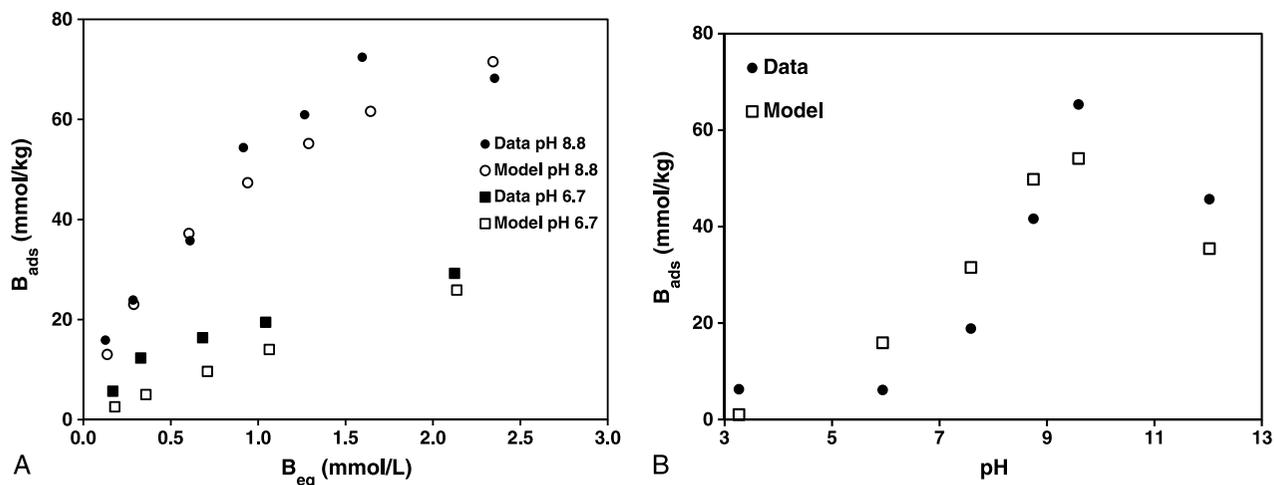


FIG. 3. Boron adsorption on humic acid HA-1 as a function of (A) equilibrium solution B concentration and (B) solution pH. Experimental data from Figures 1 to 3 of Gu and Lowe (1990) are represented by solid symbols. Constant capacitance model results are represented by open symbols.

Meyer and Bloom (1997) suggested that inclusion of B-salicylate complexation with B-catechol complexation should improve the model description, they did not carry out this calculation. In the current study, simultaneous inclusion of carboxyl and phenol sites in the constant capacitance model was able to provide a good description of B adsorption both as a function of solution pH (Fig. 4A) and equilibrium solution B concentration (Fig. 4B). Inclusion of both types of reactive surface functional groups provided a quantitative fit at pH 7 and pH 12 (Fig. 4B) where underprediction had previously been observed by Meyer and Bloom (1997).

Keren and Communar (2008, 2009) investigated B adsorption on DOM isolated from municipal sewage effluents. The B adsorption capacities of these two DOMs were lower than those obtained for humic acids by Gu and Lowe (1990), Meyer and Bloom (1997), and Lemarchand et al. (2005), which was attributed to their lower humic acid content by these authors. Keren and Communar (2009) applied a competitive adsorption model to describe B adsorption on DOM as a function of solution pH. The model simulation was successful only at high pH. After

introducing a correction factor accounting for pH dependence of DOM adsorption capacity and content of available adsorption sites, the model provided a good fit to the experimental B adsorption data (Keren and Communar, 2009). In the present study, the constant capacitance model was well able to describe B adsorption by DOM as a function of both solution pH (Fig. 5A) and equilibrium solution B concentration simultaneously (Fig. 5B). In this application, XOH_T and YOH_T were optimized with the B surface complexation constants. In agreement with the lower humic acid content of DOM, which also contains fulvic acid, the total number of reactive functional groups was smaller than for the humic acids described earlier. However, unlike for the competitive adsorption model, no correction factor for pH dependence of DOM adsorption capacity needed to be included in the constant capacitance model. The model fit to the experimental B adsorption data was excellent (Fig. 5).

Table 1 provides values for surface complexation parameters used in the constant capacitance model applications. It should be emphasized that the proton dissociation constants were held fixed at identical values, $\text{Log}K_{X^-} = -4.76$ and $\text{Log}K_{Y^-} = -10.68$, in all

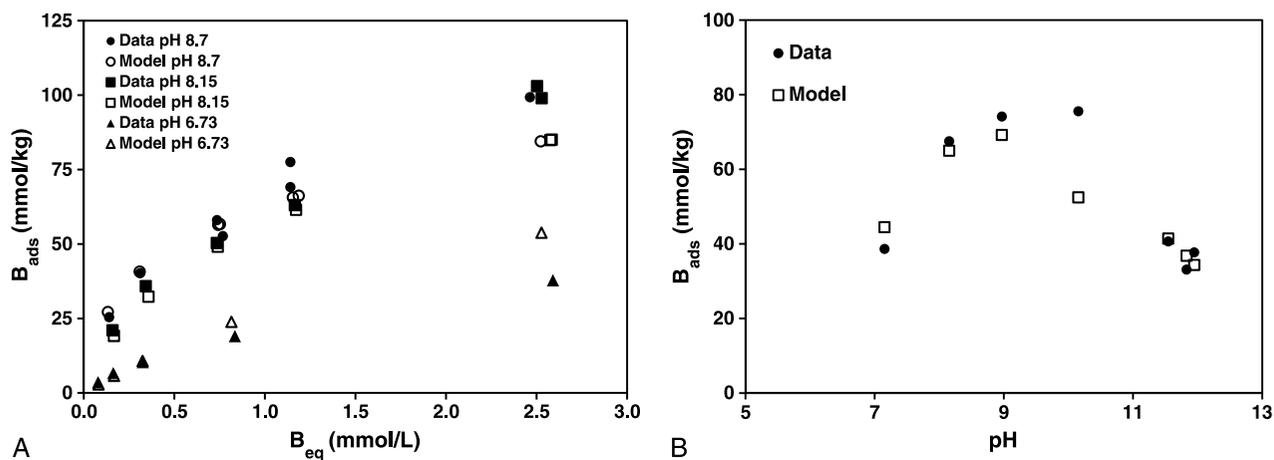


FIG. 4. Boron adsorption on humic acid as a function of (A) equilibrium solution B concentration and (B) solution pH. Experimental data from Figures 2 and 3 of Meyer and Bloom (1997) are represented by solid symbols. Constant capacitance model results are represented by open symbols.

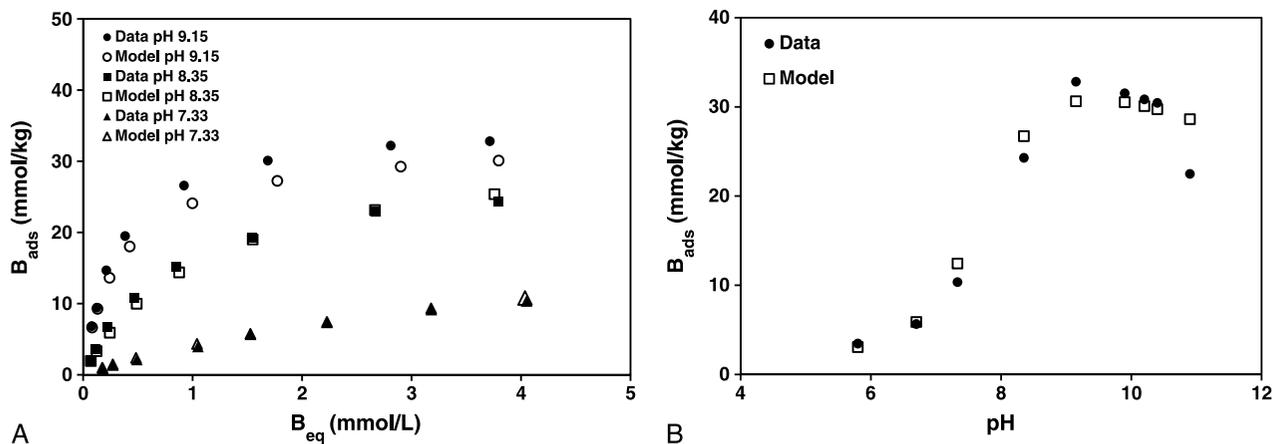


FIG. 5. Boron adsorption on DOM as a function of (A) equilibrium solution B concentration and (B) solution pH. Experimental data from Figures 1 and 2 of Keren and Communar (2009) are represented by solid symbols. Constant capacitance model results are represented by open symbols.

optimizations except for the Keren and Communar (2009) data. Values of the tetrahedral B surface complexation constants were similar in magnitude for all humic materials with an average of $\text{Log}K_{XB} = -2.58 \pm 0.54$ for the carboxyl site and $\text{Log}K_{YB} = -5.11 \pm 0.48$ for the phenol site. Predictions of B adsorption obtained using these average constants represented the experimental data less closely than the model fits but still provided a reasonable description (data not shown). These results suggest that the average surface complexation constants can be used to provide guidance for B adsorption behavior on additional humic acids.

The current application of the constant capacitance model contains the assumption that B adsorption occurs at two sets of reactive surface functional groups. Of course, humic acids are complex mixtures of a variety of functional groups. Therefore, the surface complexation constants determined in this study represent average composite values for a set of reactive carboxyl sites and a set of reactive phenol sites.

CONCLUSIONS

The constant capacitance model was used to describe B adsorption on reference Aldrich humic acid, soil humic acids from various environments, and DOM isolated from sewage effluents. The model was well able to describe the experimental B adsorption data by optimizing two tetrahedral B surface complexation constants: $\text{Log}K_{XB}$ for a carboxyl site and $\text{Log}K_{YB}$ for a phenol site. The proton dissociation constants for these sites, $\text{Log}K_X$ and $\text{Log}K_Y$, had been previously optimized by fitting the constant capacitance model to potentiometric titration data on reference Aldrich humic acid. This study represents the first time that B adsorption on a wide range of humic acids has been described using a surface complexation model. Results from the current study can be used to describe B adsorption on diverse humic materials of interest in environmental and agricultural situations.

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Cultivar and Previous Crop Effects on Methane Emissions From Drill-Seeded, Delayed-Flood Rice Production on a Silt-Loam Soil: Erratum

In the article that appeared on page 28 of the January 2014 issue the following errors occurred. The unit megagram (Mg) was replaced in several instances with milligram (mg), when the authors discussed TC and TN calculated based on bulk density and Mg in relation to grain yield as either Mg ha^{-1} or in yield-scaled units $(\text{Mg grain})^{-1}$. In the Abstract $(\text{mg grain})^{-1}$ should be $(\text{Mg grain})^{-1}$; page 30, first full paragraph: soil N and C contents (mg ha^{-1}) should be Mg ha^{-1} ; page 32, final paragraph: mg ha^{-1} should be Mg ha^{-1} (three instances); page 33, paragraph 1: $(\text{mg grain})^{-1}$ should be $(\text{Mg grain})^{-1}$ (three instances); page 34, second to last paragraph, left column: $(\text{mg grain})^{-1}$ should be $(\text{Mg grain})^{-1}$ (four instances); Table 1: TN mg ha^{-1} should be Mg ha^{-1} , TC mg ha^{-1} should be Mg ha^{-1} ; Table 3: Yield-scaled ... $(\text{mg grain})^{-1}$ should be $(\text{Mg grain})^{-1}$; Table 4: Yield-scaled... $(\text{mg grain})^{-1}$ should be $(\text{Mg grain})^{-1}$.

Reference

Rogers CW, Brye KR, Smartt AD, Norman RJ, Gbur EE, Evans-White MA. Cultivar and Previous Crop Effects on Methane Emissions From Drill-Seeded, Delayed-Flood Rice Production on a Silt-Loam Soil. *Soil Sci* 2014;179:28–36.

Retention of Nickel in Soils: Sorption–desorption and Extended X-ray Absorption Fine Structure Experiments: Erratum

In the article that appeared on page 215 of the May 2013 issue, the following errors are noted: The caption for Figure 4 was from the original draft. The caption should read: “Figure 4. Top: Ni loading on Webster reacted with 3 mM Ni for 3, 10, 30, and 45 days and Olivier soil reacted with 3 mM Ni for 45 days. Bottom: Recoveries of Ni from sequential extractions as percentages of total adsorption amounts for different soils. Different groups indicate different reaction time.” Under the Results and Discussion section, X-ray Absorption Spectroscopy subsection: In each instance in which Figure 4 is mentioned, it should be replaced with Figure 5, and vice versa.

Reference

Liao L, Roy A, Scheckel KG, Merchan G, and Selim HM. Retention of Nickel in Soils: Sorption–desorption and Extended X-ray Absorption Fine Structure Experiments. *Soil Sci* 2013;178:215–221.